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APPLICATION OF DIAMOND AND DIAMOND-LIKE CARBON FILMS AS LUBRICATING COATINGS

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Abstract

Recent work on the friction and wear properties of microwave- plasma - deposited fine grain diamond films, ion-beam-deposited diamond-like carbon (DLC) films, and rapid-thermal-annealed DLC films is reviewed. The fine grain diamond films contained about 2.5 atomic % hydrogen. The diamond grain sizes ranged from 20 to 100 nm with the preferred orientation growth of {110}. The average surface roughness (R_{rms}) of the diamond films was 15 nm. The DLC films contained about 30 atomic % hydrogen. The hydrogen content of the rapid-thermal-annealed DLC films ranged from 30 to 5 atomic % with the annealing temperature range of 350 to 1000°C. Reciprocating sliding friction experiments were conducted on the diamond, DLC, and rapid-thermal-annealed DLC films in contact with silicon nitride pins both in humid air and in dry nitrogen. Reference experiments for the friction and wear were also conducted on silicon nitride flats in contact with silicon nitride pins. The coefficients of friction for the diamond films were found to be 0.11 and 0.03 in humid air and in dry nitrogen environments, respectively. The friction coefficients of the DLC films were 0.15 and 0.01 in humid air and in dry nitrogen environments, respectively. The coefficients of friction for the diamond and DLC were considerably lower than those for the uncoated silicon nitride flats. Both diamond and DLC films had low wear factors both in humid air and in dry nitrogen environments. Thus, diamond and DLC films can be effectively used as solid lubricating coatings for ceramics such as silicon nitride. The effect of rapid-thermal-annealing on the friction for DLC films was minimal both in humid air and in dry nitrogen environments. The wear factors of the DLC films, however, were strongly dependent on the annealing temperature and moisture in the environments.

1. INTRODUCTION

As ceramics become more frequently used in engine components and wear parts, it is clear that surface modification or other means of providing acceptable levels of friction and wear will be needed. Since ceramics do not have inherently good tribological properties.[1,2] For example, the coefficients of friction higher than 0.7 were reported by Sutor and Sikra for silicon nitride sliding on itself or on M50 bearing steel.[1,2] They observed high steady-state friction accompanied by considerable wear. These studies confirm that ceramic tribological components are needed to be lubricated.

In this paper, the friction and wear properties of microwave-plasma - deposited fine grain diamond films and ion-beam-deposited DLC films, rapid-thermal-annealed (RTA) DLC films in humid air and in dry nitrogen environments were investigated. Reciprocating sliding friction experiments were conducted on the flats of diamond films, DLC films and RTA DLC films in contact with silicon nitride (Si_3N_4) pins. For comparison a similar tribological experiments were also conducted on Si_3N_4 flat with a Si_3N_4 pin.

2. EXPERIMENT

2.1 *Fine grain diamond film deposition*

Fine grain diamond film was deposited on flat surface of {100} Si substrate by a microwave chemical vapor deposition technique. Two step processes were used: first a gaseous mixture of CH_4/H_2 (8 sccm/135 sccm) was introduced at a total pressure of 5 torr for 0.63 hr with 450 W microwave power and a substrate temperature of 860°C, and followed by introducing oxygen into the system with a gaseous mixture of $CH_4/H_2/O_2$ (4 sccm/395 sccm/1 sccm) with the power of 500 W for 10.5 hr. The film thickness was varied from 0.5 µm to 1.5 µm over 10.2 cm diameter area. A detailed deposition and characterization of this fine grain diamond film was described by Wu et al.[3)]

2.2 *Diamond-like carbon film deposition*

DLC films were formed on flat surface of {100} Si substrate by direct ion beam deposition technique from a Kaufman ion source. The carbon ion beam was produced by a plasma discharge of pure CH_4. The ion impact energy was 1000 eV. The sample target was mounted on a X-Y scanner which permitted an uniform deposition over an area of 100 cm^2. The film thickness was about 300 nm. The deposition and characterization of the ion-beam-assisted DLC films were described in detail by Wu.[4)]

2.3 *Rapid-thermal-annealed diamond-like carbon film*

The rapid-thermal-annealed (RTA) DLC films were prepared by rapidly heating the DLC films inside a rapid thermal annealing apparatus in a nitrogen atmosphere for 2 minutes at various temperatures of 350, 400, 500, 600, 700, 800, 900, and 1000°C. The rapid thermal annealer used high intensity radiation to heat the sample at a rate of 300°C s^{-1}. The detailed preparation and characterization of the RTA DLC films were given by Wu et al.[5)]

2.4 *Films characterization*

The as-deposited diamond, DLC and RTA DLC films were characterized by a variety technique prior to the tribological experiment. Rutherford backscattering (RBS) and proton recoil detection (PRD) analysis were utilized to determine composition and hydrogen content of the films. Raman spectroscopy was used to characterize diamond and non-diamond carbon components. The grain size and crystal growth orientation of the films were determined from the bright- and dark-field electron microscopy and X-ray diffraction. The average surface roughness was measured by a stylus profilometer.

2.5 Friction and wear measurement

Reciprocating sliding friction experiments were conducted with the flats (Si_3N_4, diamond film, DLC film and RTA DLC films) in contact with the Si_3N_4 pins in dry nitrogen and in a humid air at a relative humidity of approximately 40 percent. Details of the friction and wear apparatus and the experimental procedures were described by Miyoshi et al.[6)] The reciprocating sliding friction experiment was begun at a load of 1 N at room temperature. The pin traveled back and forth, retracing its tracks on the flat sample, with the sliding velocity of 86 mm min^{-1} over a track length of 3 mm. The friction force was continuously monitored.

Wear groove dimensions were used to calculate the wear volume of coating removed, as well as the wear factor for the coating. The wear volume of coating was obtained from stylus profilometer tracings across the wear tracks in at least five locations, and then the average cross-sectional area of the wear track was multiplied by the wear track length (approximately 3 mm).

3. RESULTS AND DISCUSSION

3.1 Composition analysis

The fine grain diamond film consisted of about 2.5 at.% of hydrogen and 97.5 at.% of carbon. The ion-beam as-deposited DLC film was found to contain 30 at.% hydrogen and 70 at.% of carbon. The hydrogen content of the RTA DLC films was maintained at 30 at.% under the RTA temperature of 500°C. However, the hydrogen content was found to decrease linearly with the annealing temperature between 500 and 900°C, to a value of 5 at.% at 900°C. The hydrogen content of these films as a function of the annealing temperature is shown in Fig. 1. During the rapid annealing process, the carbon area density of the RTA DLC films was maintained constant. The uncertainty of the proton recoil detection analysis was on the order of ±5 at.%.

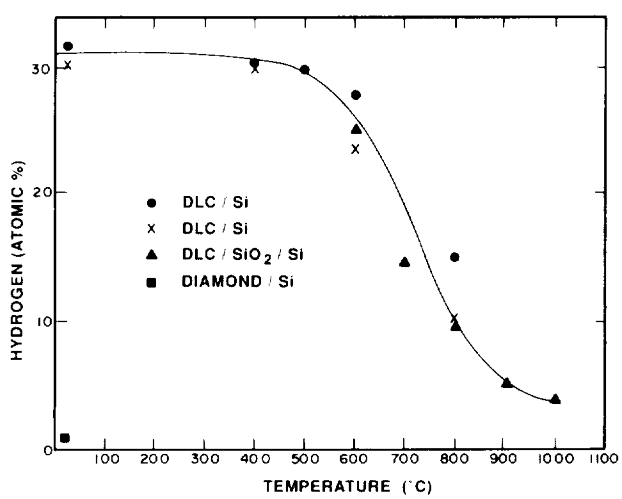

Fig. 1. Hydrogen content as a function of rapid thermal annealing temperature.

3.2 *Microstructural analysis*

The grain size of the fine grain diamond film was determined from the dark field of the transmission electron micrograph, and found to vary from 20 to 100 nm. On the other hand, the ion-beam-deposited DLC was found to be amorphous and pin-hole free.

The X-ray diffraction (XRD) pattern of the fine grain diamond film indicated that the most of diamond crystallites were orientated along {110}. The X-ray diffraction of the as-deposited DLC film was found to be amorphous, no crystal was observed.

The Raman spectra of the fine grain diamond film showed two Raman bands centered at 1333 cm^{-1} and 1500 cm^{-1}. The sharp peak at 1333 cm^{-1} was assigned as the diamond (sp^3 bonding) component of the film. The broad peak centered around 1500 cm^{-1} was attributed to the non-diamond (other forms of carbon, sp^2) component. The band assignments were done according the earlier report.[7)] The relative intensities of both the diamond and non-diamond are about the same. However, the sensitivity of the Raman technique to sp^2 bonded phase of the carbon is approximately 50 times greater than that of the sp^3 bonded phase. Thus, the peak around 1500 cm^{-1} represents a much smaller amount of non-diamond carbon.

Typical crystalline graphite shows a sharp peak at 1590 cm^{-1} (the "G" peak).[8)] If disorder is induced, the Raman spectra show an additional peak at 1350 cm^{-1} (the "D" peak). The intensity of the "D" peak increases with decreasing graphite crystal size. The spectrum of the as-deposited DLC film shows a very broad peak centered at 1539 cm^{-1}, and a very weak shoulder peak around 1340 cm^{-1}. The spectra of the RTA DLC films at 350 and 400°C are very similar to the spectrum obtained from the as-deposited DLC. No phase change in the films is observed for the RTA temperatures below 400°C, which is consistent with the present RBS and PRD data. However, the spectra which are taken from the RTA samples at 500, 600, 700, 800, 900 and 1000°C are significantly different from that of the as-deposited DLC film. As the RTA temperature increases, the full width at half maximum (FWHM) of the "G" peak narrows and the peak shifts toward the graphitic peak at 1590 cm^{-1}, indicating a transition from less tetragonal bonding to more trigonal bonding. At the same time the intensity and the FWHM of the "D" peak at 1350 cm^{-1} increase.

3.3 *Surface morphology*

The surface morphology of the films was examined by scanning electron microcopy (SEM). A relatively uniform and fine grain surface morphology was observed for the diamond film. The SEM micrographs of the DLC films and RTA DLC films showed no pin-hole with very uniform and smooth surface. The surface roughness of the diamond, DLC and RTA DLC films were measured by a surface profilometer. From a total of ten measurements, the average surface roughness were calculated to be 15 nm, 5 nm, and 5 nm, respectively for the fine grain diamond, DLC film, and RTA DLC films.

3.4 *Friction behavior*

The typical coefficients of friction for the silicon nitride flat, the diamond film, and the control DLC film in contact with silicon nitride pins obtained both in dry nitrogen and in humid air are plotted as a function of the number of repeated passes in Fig. 2.

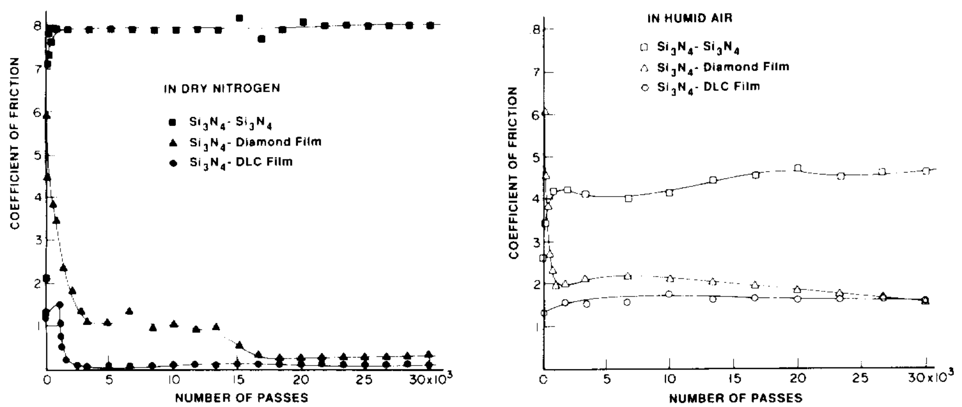

Fig. 2. Coefficients of friction as a function of number of passes for Si_3N_4 pins in contact with Si_3N_4 flat, diamond-like carbon and diamond films in dry nitrogen and in humid air.

In the dry nitrogen environment, for the silicon nitride flat contacting the silicon nitride pin, the coefficients of friction were initially low (0.22), and rapidly increased to an equilibrium value (0.8). The equilibrium coefficients of friction obtained in humid air environment were lower by a factor of about 2 (0.45) than those obtained in dry nitrogen environment. Water vapor greatly reduced friction for silicon nitride - silicon nitride contacts in humid air. This effect was the result of changing the surface chemistry in silicon nitride. It is well known that sliding action vastly increases the chemical reaction rate between silicon nitride and water vapor.[9)] These tribochemical interactions produce reaction products, such as silicon dioxide, and lead to a decrease in friction for the silicon nitride - silicon nitride contacts.

For the diamond film contacting the silicon nitride pin, the initial coefficients of friction were at 0.6 for both in the humid air and dry nitrogen environments. The high initial coefficients of friction were probably due to the plowing and microcutting actions of the higher facet tips of the diamond grains. As the sliding progressed, the coefficients of friction decreased to an equilibrium value. The equilibrium value was approximately 0.15 for the humid air environment, and 0.03 for the dry nitrogen environment at a total of 30000 passes. The sharp decreases in friction at the beginning of the experiment suggested that wear occurred on the higher facet tips of the diamond grains in the earlier repeated passes and the tips became dull. This friction behavior and the coefficients of friction in the dry nitrogen and humid air environments were found to be the same as those of the silicon nitride pin contacting the natural diamond flat.[10)]

For the DLC film contacting the silicon nitride pin in humid air, the coefficients of friction remained constant at about 0.15. However, in the dry nitrogen environment the initial coefficients of friction began at 0.13, and rapidly decreased to an equilibrium value of 0.01. The removal contaminants such as water vapor, carbon oxides, and oxide layers on the film surface is one of the possible mechanism for the decrease in friction. The equilibrium value of 0.01 is comparable with the values obtained for natural diamond and fine grain diamond film.[10)]

Higher equilibrium coefficients of friction for both diamond film and DLC film were measured in humid air than those in dry nitrogen. The rapid increase in friction in the moist environment is the results of tribochemical interaction of the Si_3N_4 pin with the moisture.

The general friction behavior as a function of number of passes for the RTA DLC films at 350, 400, 500, 600, 700, 800, 900 and 1000°C in dry nitrogen and humid air is similar to that of the as-deposited DLC film (as shown in Fig. 2). In the dry nitrogen environment, the coefficients of friction of all RTA DLC films are initially 0.15 and rapidly decrease to an equilibrium value of 0.01 within the first few passes of sliding. However, in the humid environment the coefficients of friction of all RTA DLC films again remain high at 0.15-2.0. Fig. 3 shows the equilibrium values of the coefficients of friction for Si_3N_4, diamond film, DLC film and RTA DLC films at various annealing temperatures in dry nitrogen and humid air environments.

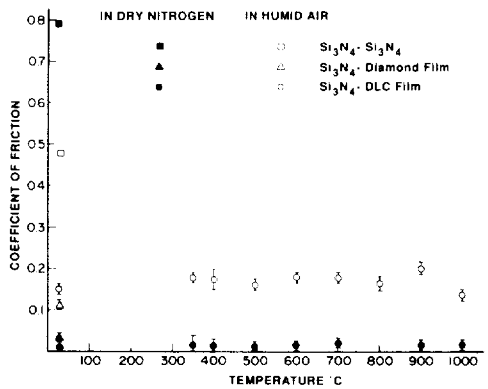

Fig. 3. Coefficients of friction in equilibrium state at various temperatures.

3.5 *Wear behavior*

The wear groove dimensions were used to calculate the volume of the fine grain diamond film, DLC, RTA DLC films and Si_3N_4 flat removed and the wear factor for these materials. Fig. 4 presents the experimental values of average wear factors of the Si_3N_4 flat, fine grain diamond film, DLC and RTA DLC films in dry nitrogen and in humid air environments.

In dry nitrogen environment, the wear factor for the Si_3N_4 was very high and calculated to be 7.0×10^{-5} mm^3/Nm The corresponding wear factors for fine grain diamond and DLC film were found to be 1.2×10^{-8}, and 6.5×10^{-8} mm^3/Nm, respectively. The wear factors of the RTA DLC films were found to be slightly increased with rapid thermal annealing temperature from 6.5×10^{-8} $mm^{3/}Nm$ at 25°C to 1.5×10^{-7} mm^3/Nm at 500°C, and rapidly decreased to 2.7×10^{-8} mm^3/Nm at 800°C, and then increased to 1.2×10^{-7} mm^3/Nm at 1000°C. All the wear factors for fine grain diamond film, DLC and RTA DLC films were lower by three order magnitude than that of Si_3N_4 flat.

In humid air environment, on the other hand, moisture significantly reduced the wear of the Si_3N_4 flat (1.0×10^{-5} mm^3/Nm), and DLC film (4.0×10^{-8} mm^3/Nm). However, moisture seemed no effect on the wear of the fine grain diamond film, but moisture significantly increased the wear factor of the RTA DLC films. As mentioned earlier, the tribochemical interactions in humid air produced a reaction product, such as silicon dioxide film, on the surface of the Si_3N_4 pin. The SiO_2 film protected the surfaces of the Si_3N_4 flat, diamond film, and DLC films so that the wear factors of these materials were lower in humid air than in dry nitrogen. The average

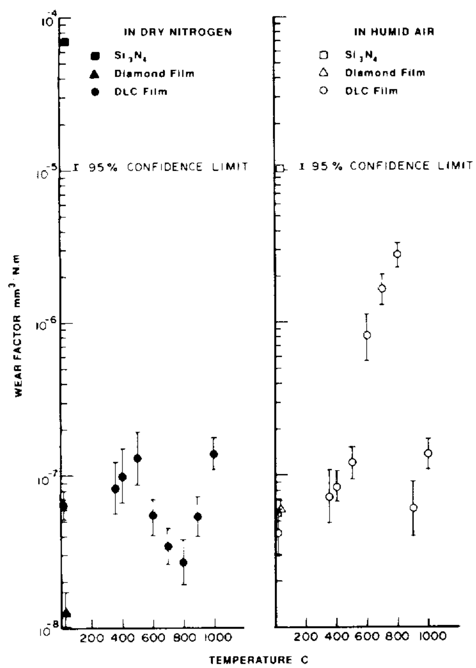

Fig. 4. Wear factors of Si_3N_4 flat, diamond film, as-deposited, and rapid-thermal-annealed DLC films in contact with Si_3N_4 pins in dry nitrogen and humid air.

wear factors of the RTA DLC films were found to increase slightly at temperatures up to 500°C. In this temperature range the wear of the RTA DLC films is not much influenced by the moisture in the environments. As shown in Fig. 1, the hydrogen content of the DLC films remains constant at 30% in this temperature range.

At annealing temperatures of 600-800°C, however, the wear of the RTA DLC films is much more susceptible to moisture. The wear factors are found to be rapidly increased with the annealing temperatures. In the humid air environment much of the film wear is due to corrosive attack by the condensed moisture on the film surface. The moisture greatly increases the film wear and consequently shortens the wear life of the films annealed in the temperature range 600-800°C. As shown in Fig. 1, the hydrogen content of the DLC films decreases dramatically with increasing RTA temperature in this region.

4. CONCLUSIONS

The equilibrium coefficients of friction of the Si_3N_4 flat in contact with Si_3N_4 pin are very high both in dry nitrogen (0.8) and in humid air environments (0.45). The wear factors in dry nitrogen (7.0×10^{-5} mm³/Nm) and in humid air (1.0×10^{-5} mm³/Nm) are also very high.

The fine grain diamond film can be produced by a low pressure and low power microwave chemical vapor deposition technique. The grain size varies from 20 to 100 nm with preferred orientation growth of {110}. The average surface roughness (R_{rms}) of the diamond films is 15 nm. Besides carbon, the film contains 2.5 at.% hydrogen. The equilibrium coefficients of friction of the diamond films in contact with Si_3N_4 pins are found to be 0.15 and 0.03 in humid air and dry nitrogen environments. The wear factors are also low both in dry nitrogen (1.2×10^{-8} mm^3/Nm) and in humid air (5.0×10^{-8} mm^3/Nm) environments.

The DLC films produced by direct high energy (1000 eV) ion beam technique are amorphous, hard, dense and pinhole free. The surface roughness (R_{rms}) of the DLC film is very smooth (5 nm). The chemical composition of as-deposited DLC is 30 at.% hydrogen and 70 at.% carbon. The coefficients of friction in dry nitrogen and humid air environments are 0.01 and 0.15, respectively. The wear factors of DLC films are also low in both environments, i.e, 6.5×10^{-8} mm^3/Nm in dry nitrogen and 4.0×10^{-8} mm^3/Nm in humid air.

The hydrogen content of the DLC films remains constant at 30% for RTA temperature from 25 to 500°C, decreases linearly from 25% to 9% at RTA temperatures in the range 600-800°C, and finally remains at 5% for RTA temperatures between 900 and 1000°C. The effect of rapid thermal annealing on the coefficients of friction of the DLC films is minimal both in humid air and in dry nitrogen environments. However, the wear factors of the DLC films are strongly dependent on the annealing temperature and moisture presence in the environment.

Thus, both the fine grain diamond films and ion-beam-assisted DLC films can be effectively used as solid lubricating coatings for ceramics such as silicon nitride in humid air and dry nitrogen environments. In the humid air environment, however, the useful temperature range for the solid lubricating DLC films is limited to 500°C.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

1. J.C. Sikra, J.E. Krysiak, P.R. Eklund, and R. Ruh, Am. Ceram. Soc. Bull., 53 (8) (1974) 581.
2. P. Sutor, Ceram. Eng. Sci. Proc., 5 (7-8) (1984) 460.
3. R.L.C.Wu, A.K. Rai, A. Garscadden, P. Kee, H. D. Desai and K. Miyoshi, J. Appl. Phys. 72 (1) (1992) 110.
4. R.L.C. Wu, Surf. Coat. Technol., 51 (1992) 258.
5. R.L.C. Wu, K. Miyoshi, R. Vuppuladhadium and H.E. Jackson, Surf. Coat. Technol., 54/55 (1992) 576.
6. K. Miyoshi and G.W.P. Rengstorff, Corrosion 45 (1989) 266.
7. K. Kobashi, K. Nishimura, V. Kawate and T. Horiuchi, Phys. Rev. B 38 (1988) 4067.
8. F. Tuinstra and K.L. Koeing, J. Chem. Phys., 53 (1970) 1126.
9. T.E. Fischer and H. Tomizawa, in K. C. Ludema (ed.), Wear of Materials, ASME, New York, (1985), p. 22.
10. K. Miyoshi, R.L.C. Wu and A. Garscadden, Surf. Coat. Technol., 54/55 (1992) 428.